

## Osmotic Pressure Measurements of Ethyl Acrylate Polymers. I. Dependence of Molecular Weight on Conversion

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Acrylic elastomers are being actively investigated for many new industrial applications because vulcanizates of these polymers exhibit unusual resistance to heat, oil, and oxygen. Little information is available regarding the solution properties of the polymers. It is the purpose of this paper to describe the results obtained for a number of polyethyl acrylate samples prepared by the solution polymerization method.

It is generally understood that the bulk, suspension, and emulsion polymerization techniques usually yield insoluble, gel-like acrylate polymers. However, in the solution polymerization method, it is possible to obtain polymers which are soluble in many solvents even though the polymers have high molecular weights. The Flory-Huggins<sup>1</sup> theory has brought considerable insight into the significance of the second term in the equation of the osmotic pressure:

$$\pi = (RT/M)C + BC^2$$

In this equation,  $B$  represents the slope of the line resulting from a plot of  $\pi/C$  versus  $C$ . The theory suggests that the slope can be expressed as

$$B = (RT/V_1 d_2^2)(1/2 - \mu)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature of the osmometer,  $M$  is the molecular weight of the solute,  $C$  is the concentration,  $V_1$  is the molar volume of the solvent,  $d_2$  is the density of the solute, and  $\mu$  is an empirical constant for the solute-solvent system.

This original derivation indicated that for a series of fractions varying solely in molecular weight a constant value of  $B$  should be obtained. However, further refinements, notably those by Flory<sup>2</sup> and Zimm<sup>3</sup> suggest that a slight dependence of the slope of the molecular weight should be evident. As pointed out by Flory,<sup>2</sup> however, this dependence on the molecular weight is so slight that it is evidently within the precision of osmotic pressure measurements. Moreover, Doty<sup>4</sup> recently indicated that the change in

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slope obtained from osmotic pressure data can be interpreted as indicating the presence of branched polymers. He investigated the thermodynamic properties of polystyrene solutions; the polymers were prepared in the presence of small amounts of divinylbenzene. The slopes of the osmotic pressure curves altered sufficiently to permit detection of one branch point per 25,000 monomer units. As Doty<sup>4</sup> pointed out, an extension of the Flory-Huggins theory suggests that a branched site may be considered a polymer-polymer contact and thereby alter the activity of the solvent. This is analogous to a poor solvent, which, as the theory reveals, should result in a lower slope. In addition, Mark and Muthana<sup>5</sup> investigated the samples of polyethylene which contained various amounts of branching. This was made evident from the study by Bryant<sup>6</sup> in which he used infrared analysis. The osmotic data clearly indicated a change in slope with a change in the extent of branching as measured by the other method.

## EXPERIMENTAL

Polymers of ethyl acrylate were prepared by the solution polymerization of the monomer;  $4.35 \times 10^{-5}$  mole per cent (0.01% wt./vol. of catalyst) of benzoyl peroxide were used (based on the amount of monomer). All polymerizations were prepared under nitrogen from which traces of oxygen had been removed by passing the gas over hot copper turnings. Except for the few bulk polymerizations, the benzene-monomer concentrations were 1.22 and 2.44 molar ratios or, on a volume basis, 1 volume of benzene to 1 volume of monomer or 2 volumes of benzene to 1 volume of monomer. The benzene, which was A.C.S. grade, was used as received. The polymerizations were stopped by precipitating the polymer in petroleum ether at room temperature. The precipitated polymer was redissolved in acetone and then reprecipitated by pouring the acetone solution into water.

The polymers were dried in an air convection oven at 40°C. for at least twenty-four hours and then dissolved in acetone for the osmotic measurements. The osmotic pressure determinations were obtained in a modified Fuoss-Mead osmometer<sup>7</sup> which contained a denitrated collodion membrane prepared as suggested by Fuoss and Mead.<sup>7</sup> The static technique was employed for all the samples, and equilibrium was usually reached within two hours. All measurements were made at 28.0°C.  $\pm$  0.005°; a water bath heated by means of an external infrared lamp was used, and the temperature was controlled by a thermoregulator mounted on a spring support.

## RESULTS

Table I is a summary of some of the osmotic data shown in Figure 1. All these polymers were prepared under the same conditions except for the extent of the reaction. The solvent-monomer concentration was 2.44 molar ratio (2 to 1 volume ratio). The osmotic pressure measurements were made on acetone solutions of the polymers.

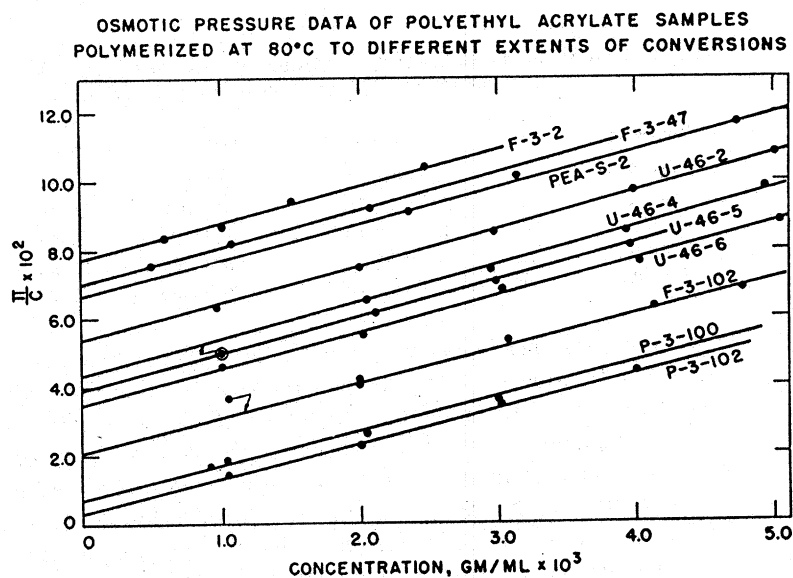


Fig. 1. Osmotic pressure data of polyethyl acrylate samples polymerized at 80°C. to different extents of conversions.

TABLE I  
MOLECULAR WEIGHT OF SAMPLES PREPARED IN THE 2 TO 1 VOLUME RATIO  
OF BENZENE TO ETHYL ACRYLATE

Sample No.	Yield, %	Intercept	Mol. wt.	Slope	
F-3-47	17	$7.04 \times 10^{-2}$	351,000	10.51	0.460
PEA-S-2	49	$6.69 \times 10^{-2}$	370,000	10.74	0.459
F-3-2	54	$7.73 \times 10^{-2}$	320,000	10.56	0.460

These data indicate that the solubility characteristics of the polymer do not change, since the slope remains substantially constant over conversions ranging from 17 to 54%. It was relatively difficult to increase the conversions above 54% at a 2.44 molar ratio of solvent to monomer. In addition, these data show a relatively constant average molecular weight over this range of conversion, and apparently under the conditions of polymerization the increase in the viscosity of the system does not affect the magnitude of the molecular weight.

The preparation of polymers by the benzene solution technique in which a 1.22 molar ratio (1:1 volume ratio) of solvent to monomer was used resulted in polymers completely soluble in acetone. The results are also represented in Figure 1, and a summary of the pertinent data is given in Table II.

The results in Table II indicate that the ethyl acrylate monomer readily polymerizes to extremely high molecular weight polymers which are soluble in organic solvent. The slopes are approximately the same over the conversion range of 11 to 86%, and, furthermore, these values agree closely with those obtained by using a 2.44 molar ratio of benzene to monomer.

TABLE II  
MOLECULAR WEIGHT OF SAMPLES PREPARED IN THE 1 TO 1 VOLUME RATIO  
OF BENZENE TO ETHYL ACRYLATE

Sample No.	Yield, %	Intercept	Mol. Wt.	Slope	$\mu$
U-46-2	11	$5.41 \times 10^{-2}$	456,000	10.61	0.460
U-46-4	33	$4.35 \times 10^{-2}$	568,000	10.68	0.459
U-46-5	52	$3.91 \times 10^{-2}$	632,000	10.76	0.459
U-46-6	64	$3.49 \times 10^{-2}$	708,000	10.59	0.460
F-3-103	86	$2.01 \times 10^{-2}$	1,200,000	10.28	0.461

There is a significant increase of molecular weight with conversion, which was not noticeable for the polymers prepared in the 2.44 molar ratio of solvent to monomer. Evidently the effect of viscosity upon the termination reaction is much more pronounced for this concentration of benzene in the polymerization mixture than for the concentration discussed earlier. The molecular weights range from about 456,000 at low conversions to more than 1,000,000 at high conversions. Since these are average molecular weight values, a fraction of the high conversion polymer must be extremely high, about of the order of 10,000,000. These data substantiate the view that the ethyl acrylate free radical is extremely stable, which can partly be explained by resonance, and therefore does not exhibit any appreciable tendency to chain transfer to monomer or solvent. In addition, since all these samples resulted in parallel slopes, it is believed that chain transfer to polymer is also negligible.

As would be anticipated from these results, ethyl acrylate polymerized in the absence of solvent would have such an extremely high molecular weight that for all practical purposes it could be considered a gel. Osmotic pressure data are presented for polymers polymerized at 80°C. in bulk in the absence of added catalyst. The data in Table III are a summary of the data obtained from Figure 1.

TABLE III  
MOLECULAR WEIGHT OF SAMPLES PREPARED WITHOUT A SOLVENT

Sample No.	Yield, %	Intercept	Mol. wt.	Slope	$\mu$
P-3-100	4.4	$0.68 \times 10^{-2}$	3,600,000	10.12	0.461
P-3-102	18	$0.31 \times 10^{-2}$	8,000,000	10.36	0.461

All attempts to obtain soluble polymers at higher conversions resulted in an insoluble product. These results indicate, however, that a soluble polymer can be obtained at low conversions and that the number-average molecular weights of these polymers are of the order of several million. In addition, these slopes correspond well with the values obtained for the polymers prepared in benzene solution at the same temperature. Huggins<sup>8</sup> and Alfrey, Bartovics, and Mark<sup>9</sup> have suggested that the solvent-polymer interaction may be dependent upon the internal architecture of the polymer mol-

ecule as it is formed during the polymerization process. Since the slopes or  $\mu$  values obtained for the polymers prepared in benzene solution as well as in bulk at 80°C. are significantly the same, one can infer that the monomer units in the polymer chains have the same random arrangements. Therefore, provided the ethyl acrylate polymers are polymerized at the same temperature, it can be anticipated that they will exhibit the same polymer-solvent interaction or, in other words, the solutions of the polymers will have the same value for  $\mu$ . These results suggest that the chain transfer process to polymer, which can ultimately lead to the formation of a branched molecule, is not a significant reaction. The fact that the osmotic pressure curves are parallel indicates that the osmotic pressure method does not reveal any change in the polymer-solvent interaction and implies that the insolubility of ethyl acrylate polymers prepared in bulk and emulsion is predominantly due to the extremely high molecular weights of these polymers.

### SUMMARY

By employing the solution polymerization method, ethyl acrylate was readily polymerized, giving a product soluble in a number of organic solvents. By using benzene as the solvent, polymers of exceptionally high molecular weights were produced. The polymer samples were obtained by precipitation after the polymerization had proceeded for various periods of time. The slopes of the osmotic pressure curves were substantially constant for all the polymers. It is concluded that chain transfer to polymer during the polymerization process is insignificant and that the ethyl acrylate polymers do not contain any branched sites. It can be inferred from these data that the insolubility of ethyl polyacrylates frequently encountered is predominantly due to the extremely high molecular weights of the polymers.

### References

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### Résumé

En utilisant la méthode de polymérisation en solution, on obtient un acrylate d'éthyle polymérisé, soluble dans un grand nombre de solvants organiques. En utilisant le benzène comme solvant, on obtient des polymères de poids moléculaires exceptionnellement élevés. Les échantillons de polymères sont isolés par précipitation, lorsque la polymérisation a duré un temps déterminé. Les tangentes aux courbes de pression osmotique sont remarquablement constantes pour tous les polymères. On en conclut que

les réactions de transfert de chaîne au polymère sont insignifiantes au cours de la polymérisation, et que les polyacrylates d'éthyle forment des polymères rectilignes, non-branchés. On conclut également de ces résultats que l'insolubilité des polyacrylates d'éthyle, fréquemment rencontrée, est principalement due au poids moléculaire extrêmement élevé des polymères obtenus.

### **Zusammenfassung**

Unter Anwendung der Methode der Lösungspolymerisation wurde Athylacrylat leicht polymerisiert, und es entstand ein in verschiedenen organischen Lösungsmitteln lösliches Produkt. Bei Benutzung von Benzol als Lösungsmittel wurden Polymere von aussergewöhnlich hohem Molekulargewicht gebildet. Die Polymerprodukte wurden durch Fällung erhalten, nachdem die Polymerisation für verschieden lange Zeitspannen fortgeschritten war. Die Neigung der osmotischen Druck-Kurven war in der Hauptsache für alle Polymere konstant. Es wird daraus geschlossen, dass Kettenübertragung während des Polymerisationsvorganges unerheblich ist, und dass das Athylacrylat-Polymere keinerlei Verzweigungsstellen enthält. Es kann diesen Daten entnommen werden, dass die oft in Athylpolyacrylaten angetroffene Unlöslichkeit vor allem durch die ausserordentlich hohen Molekulargewichte der Polymeren bedingt ist.